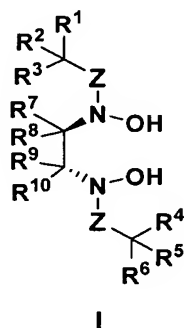


## CLAIMS:

1. A method of performing a catalytic asymmetric oxidation comprising:  
reacting a substrate with catalytic amounts of a chiral bishydroxamic acid  
ligand and a metal, in the presence of an oxidation reagent, to produce a  
chiral oxidation product.

2. The method of claim 1, where the chiral bishydroxamic acid ligand  
has a structure I:



where:

$R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ , and  $R^6$  are each independently selected from  
the group consisting of hydrogen, alkyl, cycloalkyl, alkoxy,  
alkylamino, heterocyclyl, aryl, heteroaryl, and arylalkyl;

or where  $R^1$  and  $R^2$ , together with the atom to which they  
are attached, form a substituted or unsubstituted ring selected  
from the group consisting of cycloalkyl, heterocyclyl, or aryl;

or where  $R^4$  and  $R^5$ , together with the atom to which they  
are attached, form a substituted or unsubstituted ring selected  
from the group consisting of cycloalkyl, heterocyclyl, and aryl;

$R^7$ ,  $R^8$ ,  $R^9$ , and  $R^{10}$  are each independently selected from the  
group consisting of hydrogen, alkyl, cycloalkyl, alkoxy,  
alkylamino, heterocyclyl, aryl, heteroaryl, and arylalkyl;

or where  $R^7$  and  $R^9$ , together with the atoms to which they are attached, form a substituted or non-substituted ring selected from the group consisting of cycloalkyl and heterocyclyl;

—Z— is selected from the group consisting of —C(O)— and —S(O)<sub>2</sub>—.

3. The method of claim 1, where the metal is selected from the group consisting of vanadium (IV), vanadium (V), molybdenum (IV), molybdenum (V), and molybdenum (VI).

4. The method of claim 3, where the metal is selected from the group consisting of vanadium (IV) and vanadium (V).

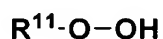
5. The method of claim 3, where the metal is selected from the group consisting of molybdenum (IV), molybdenum (V), and molybdenum (VI).

6. The method of claim 1 wherein the substrate is selected from the group consisting of sulfide, phosphine, alkene, and cyclic alkene.

7. The method of claim 6, where the substrate is selected from the group consisting of sulfide and phosphine.

8. The method of claim 6, where the substrate is selected from the group consisting of alkene and cyclic alkene.

9. The method of claim 1, where the oxidation reagent is an organic hydroperoxide with the following structure (II):



II

where,  $R^{11}$  is selected from the group consisting of alkyl, cycloalkyl, aryl, heteroaryl, and heterocyclyl.

10. The method of claim 1 wherein the chiral oxidation product has a structure III:



III

where,

Y is selected from the group consisting of sulfides and phosphines.

11. The method of claim 2, where the substrate is an alkene or cyclic alkene.

12. The method of claim 2, where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> are each independently selected from the group consisting of hydrogen, alkyl, alkoxy, and alkylamino.

13. The method of claim 2, where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> are each independently selected from the group consisting of cycloalkyl and heterocyclyl.

14. The method of claim 2, where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> are each independently selected from the group consisting of aryl, arylalkyl, heteroaryl, and halogen.

15. The method of claim 2, where:

R<sup>1</sup> and R<sup>2</sup>, together with the atom to which they are attached, form a substituted or unsubstituted ring;

R<sup>4</sup> and R<sup>5</sup>, together with the atom to which they are attached, form a substituted or unsubstituted ring; and

the ring formed by R<sup>1</sup> and R<sup>2</sup> is identical to the ring formed by R<sup>4</sup> and R<sup>5</sup>.

16. The method of claim 2, where  $R^7$ ,  $R^8$ ,  $R^9$ , and  $R^{10}$  are each independently selected from the group consisting of hydrogen, alkyl, alkoxy, and alkylamino.

17. The method of claim 2, where  $R^7$ ,  $R^8$ ,  $R^9$ , and  $R^{10}$  are each independently selected from the group consisting of cycloalkyl and heterocyclyl.

18. The method of claim 2, where  $R^7$ ,  $R^8$ ,  $R^9$ , and  $R^{10}$  are each independently selected from the group consisting of aryl, arylalkyl, and heteroaryl.

19. The method of claim 2, where  $R^7$  and  $R^9$ , together with the atoms to which they are attached, form a ring.

20. The method of claim 19, where  $R^8$  and  $R^{10}$  are identical.

21. The method of claim 17, where  $R^7$  and  $R^9$ , together with the atoms to which they are attached, form a ring.

22. The method of claim 21, where  $R^8$  and  $R^{10}$  are identical.

23. The method of claim 2, where:

$R^1$  and  $R^2$  are aryl groups;

$R^3$  is hydrogen;

$R^4$  and  $R^5$  are aryl groups; and

$R^6$  is hydrogen.

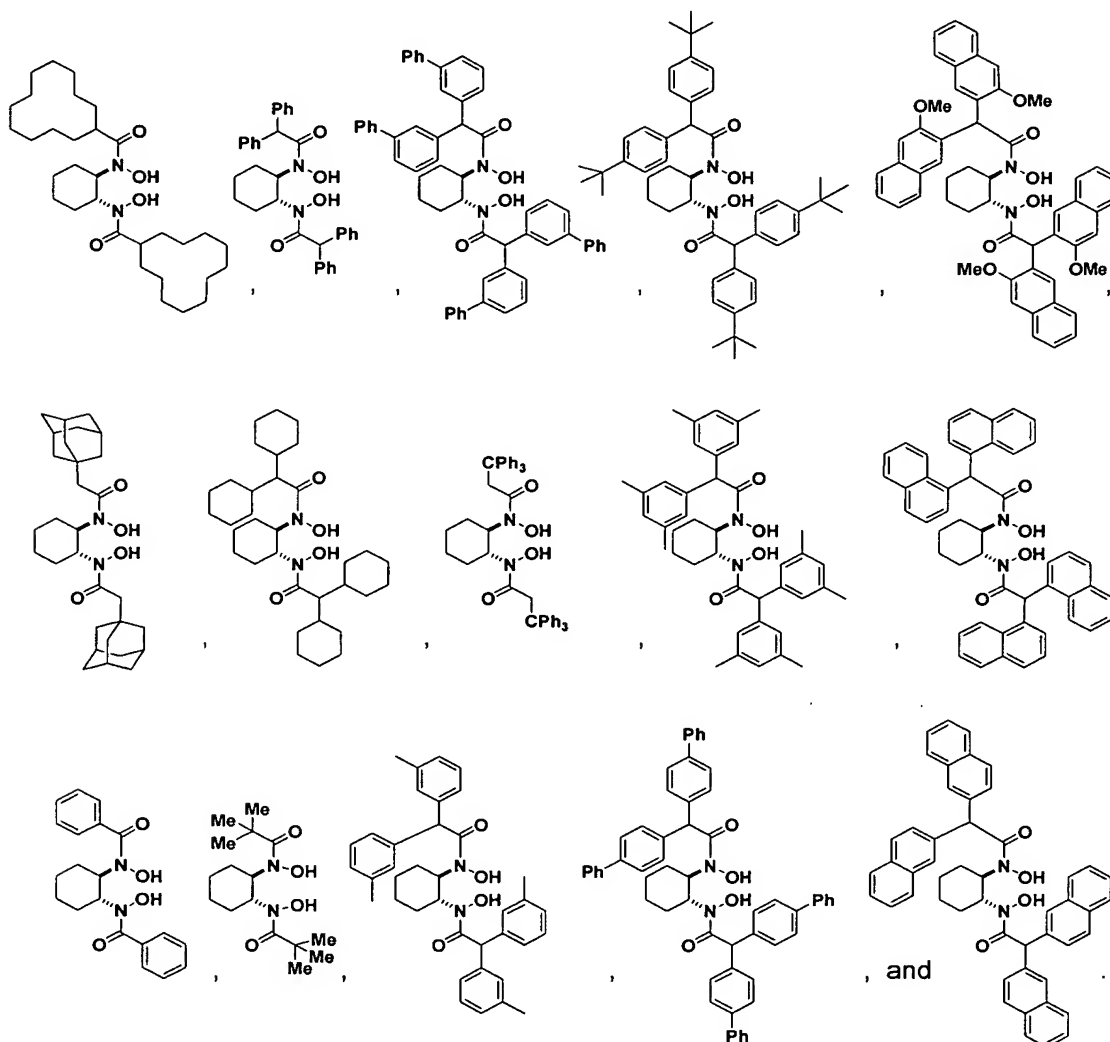
24. The method of claim 23, where:

$R^1$  and  $R^2$  are identical; and

$R^4$  and  $R^5$  are identical.

25. The method of claim 24, where  $R^1$ ,  $R^2$ ,  $R^4$ , and  $R^5$  are identical.

26. The method of claim 2, where the chiral bishydroxamic acid ligand (I) is selected from the group consisting of:



27. The method of claim 6, where the metal is selected from the group consisting of vanadium (IV) and vanadium (V).

28. The method of claim 8, where the metal is selected from the group consisting of molybdenum (IV), molybdenum (V), and molybdenum (VI).

29. The method of claim 3, where the metal is selected from the group consisting of  $\text{VO}(\text{OPr}^f)_3$ ,  $\text{VO}(\text{acac})_2$ ,  $\text{VO}(\text{OEt})_3$ , and  $\text{MoO}_2(\text{acac})_2$ .

30. The method of claim 8, where the metal is selected from the group consisting of  $\text{VO}(\text{OPr})_3$ ,  $\text{VO}(\text{acac})_2$ ,  $\text{VO}(\text{OEt})_3$ , and  $\text{MoO}_2(\text{acac})_2$ .

31. The method of claim 9, where the organic hydroperoxide is selected from the group consisting of tert-butyl hydroperoxide and cumene hydroperoxide.

32. The method of claim 9, where the organic hydroperoxide is tert-butyl hydroperoxide.

33. The method of claim 9, where the organic hydroperoxide is cumene hydroperoxide.

34. The method of claim 8, where the oxidation reagent is selected from the group consisting of tert-butyl hydroperoxide and cumene hydroperoxide.

35. The method of claim 8, where the oxidation reagent is tert-butyl hydroperoxide.

36. The method of claim 8, where the oxidation reagent is cumene hydroperoxide.

37. The method of claim 1, where the oxidation reagent is hydrogen peroxide.

38. The method of claim 8, where the oxidation reagent is hydrogen peroxide.

39. A method of preparing a chiral bishydroxamic acid ligand comprising:

condensing an optically active 1,2-diammonium tartarate with p-anisaldehyde to provide a di-imine;  
oxidizing the di-imine to produce a dioxaziridine;

hydrolyzing the dioxadirizine to generate a dihydroxylamine hydrochloride;

silylating the dihydroxylamine hydrochloride to provide a silyl protected dihydroxylamine;

condensing the silyl protected dihydroxylamine with an acid chloride to produce the chiral bishydroxamic acid ligand.

40. The method of claim 39, where the chiral bishydroxamic acid ligand is prepared by a method comprising:

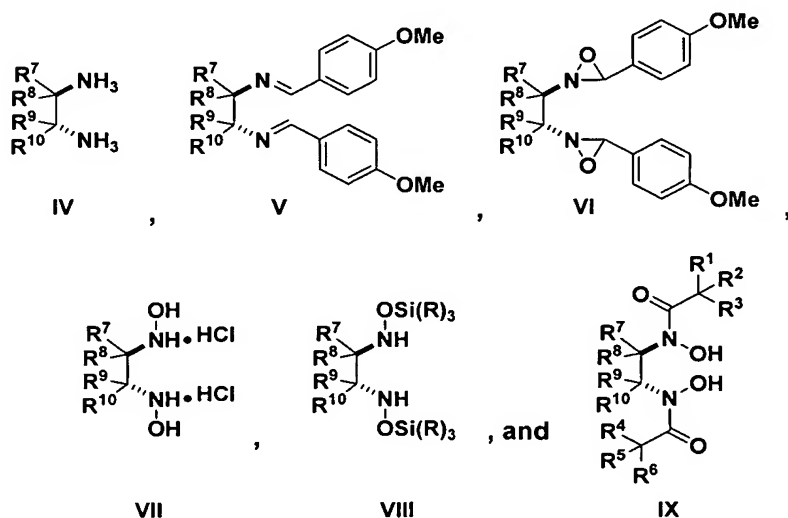
condensing an optically active 1,2-diammonium tartrate (IV) with p-anisaldehyde to provide a di-imine (V);

oxidizing the di-imine (V) to produce a dioxadirizine (VI);

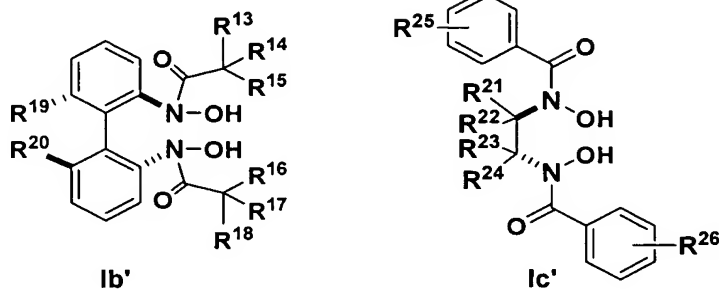
hydrolyzing the dioxadirizine (VI) to generate a dihydroxylamine hydrochloride (VII);

silylating the dihydroxylamine hydrochloride (VII) to provide a silyl protected dihydroxylamine (VIII);

condensing the silyl protected dihydroxylamine with an acid chloride to produce the bishydroxamine acid (IX).



41. The method of claim 1, where the chiral bishydroxamic acid ligand (I) is selected from the following formulae:



where:

R<sup>13</sup>, R<sup>14</sup>, R<sup>15</sup>, R<sup>16</sup>, R<sup>17</sup>, and R<sup>18</sup> are each independently selected from the group consisting of hydrogen, alkyl, cycloalkyl, alkoxy, alkylamino, heterocyclyl, aryl, heteroaryl, and arylalkyl;

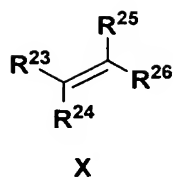
R<sup>19</sup> and R<sup>20</sup> are each independently selected from the group consisting of hydrogen, halogen, alkyl, cycloalkyl, alkoxy, alkylamino, heterocyclyl, aryl, heteroaryl, and arylalkyl;

R<sup>21</sup>, R<sup>22</sup>, R<sup>23</sup>, and R<sup>24</sup> are each independently selected from the group consisting of hydrogen, alkyl, cycloalkyl, alkoxy, alkylamino, heterocyclyl, aryl, heteroaryl, and arylalkyl;

R<sup>25</sup> and R<sup>26</sup> are each independently selected from the group consisting of hydrogen, halogen, alkyl, cycloalkyl, alkoxy, alkylamino, heterocyclyl, aryl, heteroaryl, and arylalkyl.

42. The method of claim 8, where the alkene is of the formula (X):

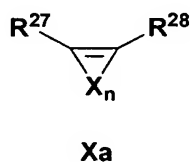




where:

$R^{23}$ ,  $R^{24}$ ,  $R^{25}$ , and  $R^{26}$  are each independently selected from the group consisting of hydrogen, halogen, alkyl, cycloalkyl, alkoxy, alkylamino, heterocyclyl, aryl, heteroaryl, and arylalkyl.

43. The method of claim 8, where the alkene is a cyclic alkene of the formula (**Xa**):



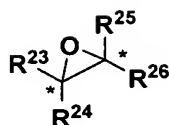
where:

$R^{27}$  and  $R^{28}$  are each independently selected from the group consisting of hydrogen, alkyl, cycloalkyl, alkoxy, alkylamino, heterocyclyl, aryl, aralkyl, heteroaryl, halogen, and alkene;  
 $n$  is 1, 2, 3, 4, 5, 6, or 6;

each  $X$  is independently selected from the group consisting of —  
 $CR'R''$ , — $NR'$ —, and — $O$ —;

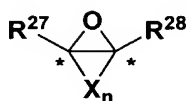
$R'$  and  $R''$  are each independently selected from the group consisting of hydrogen, alkyl, cycloalkyl, alkoxy, alkylamino, heterocyclyl, aryl, aralkyl, heteroaryl, and halogen.

44. The method of claim 42, where the chiral oxidation product is of the for formula (**Xb**):



**Xb**

45. The method of claim 43, where the chiral oxidation product is of the formula (**Xc**):



**Xa**

46. The method of claim 1, where the reacting step is carried out in a solvent.

47. The method of claim 46, where the reacting step is carried out in a solvent selected from the group consisting of methylene chloride, toluene, chloroform, and ethyl acetate.

48. The method of claim 1, where the reacting step is carried out at a temperature of about -20 to about 25 °C.

49. The method of claim 1, where the reaction is carried out with about 0.001 to about 0.1 equivalents of the chiral bishydroxamic acid ligand (I).

50. The method of claim 1, where the reaction is carried out with about 0.005 to about 0.05 equivalents of metal.